SUBSTITUTE SPECIFICATION

PRODUCTION METHOD OF MATERIAL FILM AND PRODUCTION APPARATUS OF MATERIAL FILM

TECHNICAL FIELD

[0001] The present invention relates to a production method and a production apparatus for irradiating plasma or vapor including irradiating atoms, irradiating molecules, or the like onto a material such as fullerene, carbon nanotube, or the like within a vacuum vessel, thereby producing encapsulating-fullerene, hetero-fullerene, or encapsulating-nanotube.

BACKGROUND ART

[0002] Patent-Unrelated Reference 1: "Nature and Application of Fullerene Plasma", Journal of Plasma/Nuclear Fusion Academic Society, Vol. 75, No. 8, pp. 927-933, 1999 August

Patent-related reference 1: Japanese Patent Application No. 2004-001362

[0003] Encapsulating-fullerenes are materials which are made of spherical clusters of carbon molecules known as fullerenes and encapsulation target atoms such as alkali metal encapsulated therein, and which are expected to be applied to electronics, medical treatment, and the like. Known as a production method of encapsulating-fullerene is

a method (patent-unrelated reference 1) configured to shoot alkali metal vapor to a hot plate heated within a vacuum vessel to thereby generate plasma, and to inject fullerene vapor into the generated plasma flow, thereby depositing encapsulating-fullerene on a deposition-assistance substrate arranged downstream of the plasma flow.

[0004] Shooting the alkali metal gas generated by a sublimation oven onto the heated hot plate, generates alkali metal plasma including alkali metal ions and electrons by contact ionization. The generated plasma is confined within the vacuum vessel by a uniform magnetic field formed by an electromagnetic coil arranged around a vacuum chamber, and is established into a plasma flow flowing in the magnetic field direction from the hot plate. Injected into the plasma flow is fullerene vapor comprising C_{60} by a fullerene sublimation oven arranged in the course of the plasma flow, so that electrons constituting the plasma flow attach to C_{60} having a larger electron affinity, thereby generating negative ions of C_{60}. As a result, the plasma flow is brought into alkali metal/fullerene plasma mixedly including therein positive ions of the alkali metal, negative ions of fullerene, and residual electrons, based on the following reactions in case of adoption of lithium as the alkali metal, for example:

$Li \rightarrow Li^{+} + e^{-}$

$C_{60} + e^{-} \rightarrow C_{60}^{-}$

There is arranged a deposition-assistance substrate

downstream of such a plasma flow and the deposition-assistance substrate is brought to have a positive bias voltage applied thereto, so that alkali metal ions having smaller masses are decelerated and fullerene ions having larger masses are accelerated to increase interaction between alkali metal ions and fullerene ions in a manner that alkali metal ions and fullerene ions collide with one another by an action of coulomb attractive forces therebetween, resulting in production of encapsulating-fullerene.

(Fullerene-Plasma Reaction Scheme)

[0005] To cause an atom to be encapsulated in a cage of a fullerene molecule, it is required to collide an encapsulation target atom with fullerene by a relatively large energy. However, excessively higher collision energies between an encapsulation target atom and a fullerene molecule lead to breakage of the fullerene molecule, whereas excessively lower collision energies rarely lead to encapsulation. Thus, to improve a production efficiency of encapsulating-fullerenes, it is insufficient to merely improve a collision probability, and it is further required to control a collision energy. Although it has been possible to control a collision probability by virtue of the conventional encapsulating-fullerene production method based on the fullerene/plasma reaction scheme, it has been impossible to control a collision energy.

[0006] As such, the present inventors have devised: in a scheme where alkali metal plasma is irradiated to a deposition-assistance substrate and fullerene vapor is simultaneously shot toward the deposition-assistance substrate, or where alkali metal plasma is irradiated to a fullerene film previously deposited on a deposition-assistance substrates; to apply a negative bias voltage to the deposition-assistance substrate and control the bias voltage to thereby give acceleration energies to alkali metal ions, thereby irradiating alkali metal ions into a fullerene film (ion irradiation scheme). This allows collision energies between encapsulation target atoms and fullerene to be controlled by the bias voltage applied to the deposition-assistance substrate. This technique has been filed as a patent application according to the patent-related reference 1. Nonetheless, this technique has not been yet laid open to public inspection as of the filing date of this patent application, and thus is not a known technique.

[0007] FIG. 13 is a cross-sectional view of a material film production apparatus according to the background art of the present invention. The production apparatus according to the background art is constituted of a vacuum vessel 301, an electromagnetic coil 303, means for generating plasma of alkali metal as an encapsulation target atom, a deposition-assistance substrate 316, and a bias voltage control power supply 318. The vacuum vessel

301 is evacuated to a degree of vacuum of about 10^{-4}Pa by a vacuum pump 302. The alkali metal plasma generation means is constituted of a heating filament 304, a hot plate 305, an alkali metal sublimation oven 306, and an alkali metal gas introduction pipe 307. When the alkali metal vapor generated by the sublimation oven 306 is shot to the hot plate 305 from the alkali metal gas introduction pipe 307, alkali metal atoms are ionized on the high-temperature hot plate and thermoelectrons are simultaneously discharged from the hot plate, thereby generating plasma including alkali metal ions and electrons. The thus generated plasma is confined within a magnetic field direction within the vacuum vessel 301 along a uniform magnetic field formed by the electromagnetic coil 303, and established into a plasma flow 310 flowing from the hot plate 305 toward a deposition-assistance substrate 316.

[0008] Applied to the deposition-assistance substrate 316 is a negative bias voltage by the bias voltage control power supply 318. Alkali metal ions in the plasma are provided with acceleration energies by the bias voltage applied to the deposition-assistance substrate, and irradiated toward the deposition-assistance substrate. Simultaneously, fullerene is sublimated by a fullerene sublimation oven 313, and shot to the deposition-assistance substrate 316 from a fullerene gas introduction pipe 314. Alkali metal ions collide with fullerene molecules on the deposition-assistance substrate 316 or near the deposition-

assistance substrate 316, thereby producing alkali-metal-encapsulating fullerene.

DISCLOSURE OF THE INVENTION

Problem to be solved by the Invention

[0009] According to the production method of the background art, it is possible to precisely control a collision energy (acceleration energy) of the factors (collision probability and collision energy) which govern a production efficiency of encapsulating-fullerene, by the bias voltage to be applied to the deposition-assistance substrate. In turn, control of collision probability has been conducted by controlling a density of alkali metal ions or a density of fullerene molecules, by temperature setting of each sublimation oven. Higher sublimation temperatures lead to larger sublimation amounts of alkali metal or fullerene to thereby increase ion densities or molecular densities thereof, thereby allowing an increased collision probability. However, since there is required a longer time up to obtainment of a stabilized temperature in case of the control based on sublimation temperature, and sublimation amounts depend on not only sublimation temperatures but also a residual amount of material filled in the applicable oven, an amount of material solidified on the introduction pipe and accumulated thereon, and the like, it has been difficult to precisely control sublimation amounts by controlling sublimation temperatures,

respectively.

[0010] In turn, since there has been such a problem that a generation reaction of hydrogenated fullerene is promoted when a density of alkali metal ions is high as compared with a density of fullerene molecules such that a production efficiency of encapsulating-fullerene is deteriorated, it has been required to precisely control an ion density so as to also restrict generation of hydrogenated fullerene.

[0011] Moreover, the conventional fullerene/plasma reaction scheme and the ion irradiation scheme according to the background art have each been accompanied by such a problem that it is difficult to irradiate a relatively large encapsulation target atom into fullerene.

[0012] FIG. 14 is a view showing collision between particles in an attempt to form encapsulating-fullerene by irradiating a K ion as an encapsulation target atom into an empty fullerene molecule comprising C_{60} by the production apparatus according to the background art. The K ion is provided with an acceleration energy by the negative bias voltage applied to the deposition-assistance substrate, and is moved toward the fullerene molecule (FIG. 14(a)). Although the collision of the K ion with the fullerene molecule leads to deformation of a cage, the deformation is not so large because of a relatively small mass of the K ion. Additionally, since C_{60} includes six-membered rings having an averaged diameter of 2.48Å whereas a K ion has a

diameter of 2.76Å such that C_{60} has openings each smaller than the K ion, the fullerene molecule is only slightly deformed in most cases even by collision of the K ion therewith (FIG. 14(b)) resulting in that the K ion is not encapsulated in the fullerene molecule (FIG. 14(c)).

[0013] Sizes of encapsulation target atom ions vary depending on kinds of encapsulation target atom. In case of alkali metals, since Li, Na and the like each have a smaller ion diameter and provide higher encapsulation probabilities even by the ion irradiation scheme by the background art, it is possible to generate a relatively large amount of encapsulating-fullerene. However, such a scheme has failed to obtain a sufficiently higher encapsulation probability, even when attempting to encapsulate larger ions such as K, Rb and the like.

[0014] Further, encapsulating-fullerene is rarely formed in case of relatively large encapsulation target atoms such as K, Rb, and the like, particularly in case of a lower acceleration energy for ion irradiation. Contrary, in case of higher acceleration energies, for example, when a K ion is irradiated to a deposited fullerene film at an acceleration energy of 80eV, the deposited fullerene film is problematically broken due to sputtering. Thus, there has been such a problem that an optimum condition for an acceleration energy for forming encapsulating-fullerene is not obtained even by higher and lower energies.

Means for solving the Problem

[0015] The present invention (1) resides in a material film production method, characterized in that the method comprises the steps of:

generating plasma including irradiating ions;

applying a control voltage to an electric potential body in contact with the plasma to thereby control a density of the irradiating ions;

irradiating the plasma toward a deposition-assistance substrate;

applying a bias voltage of a polarity opposite to that of the irradiating ions to the deposition-assistance substrate, to thereby provide the irradiating ions with acceleration energies, respectively; and

irradiating the irradiating ions into a material film.

[0016] The present invention (2) resides in the material film production method of invention (1), characterized in that the method further comprises the step of:

measuring an electric current flowing between the deposition-assistance substrate and a bias power supply for applying the bias voltage thereto, to thereby measure the density of the irradiating ions.

[0017] The present invention (3) resides in a material film production method, characterized in that the method comprises the steps of:

generating plasma including encapsulation target ions

and collision ions having the same polarity as the encapsulation target ions;

irradiating the plasma toward a deposition-assistance substrate;

applying a bias voltage of a polarity opposite to that of the encapsulation target ions to the deposition-assistance substrate, to thereby provide the encapsulation target ions and collision ions with acceleration energies, respectively; and

colliding the collision ions with material molecules constituting a material film, to thereby cause the material molecules to encapsulate the encapsulation target ions, respectively.

[0018] The present invention (4) resides in the material film production apparatus of any one of inventions 1 through 3, characterized in that the method further comprises the step of:

depositing the material film on the deposition-assistance substrate, simultaneously with the irradiation of the plasma toward the deposition-assistance substrate.

[0019] The present invention (5) resides in the material film production method of any one of inventions 1 through 3, characterized in that the method further comprises the step of:

irradiating the plasma onto the material film previously deposited on the deposition-assistance substrate.

[0020] The present invention (6) resides in a

material film production method, characterized in that the method comprises the steps of:

generating plasma including collision ions;

irradiating the plasma toward a material film previously deposited on the deposition-assistance substrate;

simultaneously therewith, shooting vapor comprising encapsulation target molecules toward the material film;

colliding the collision ions with material molecules constituting the material film; and

simultaneously therewith, causing the material molecules to encapsulate the encapsulation target molecules, respectively.

[0021] The present invention (7) resides in the material film production method of any one of inventions 1 through 6, characterized in that the method further comprises the step of:

transporting the generated plasma by a magnetic field to thereby irradiate the plasma toward the deposition-assistance substrate.

[0022] The present invention (8) resides in the material film production method of any one of inventions 1 through 7, characterized in that the material film is a film comprising fullerene or nanotube.

[0023] The present invention (9) resides in the material film production method of any one of inventions 1 through 5, 7, and 8, characterized in that the irradiating

ions or the encapsulation target ions are alkali metal ions, nitrogen ions, or halogen ions.

[0024] The present invention (10) resides in the material film production method of any one of inventions 6 through 8, characterized in that the encapsulation target substance is TTF, TDAE, TMTSF, Pentacene, Tetracene, Anthracene, TCNQ, Alq_3, or F_4TCNQ.

[0025] The present invention (11) resides in the material film production method of any one of inventions 3 through 10, characterized in that the collision ions each have a diameter of 3.0Å or larger.

[0026] The present invention (12) resides in the material film production method of invention 11, characterized in that the collision ions are fullerene positive ions or fullerene negative ions, respectively.

[0027] The present invention (13) resides in a material film production apparatus comprising:

a vacuum vessel;

magnetic field generation means;

plasma generation means for generating plasma including irradiating ions;

an electric potential body configured to control a density of the irradiating ions by applying a control voltage to the electric potential body;

a deposition-assistance substrate for depositing a material film thereon; and

a bias power supply configured to apply a bias

voltage to the deposition-assistance substrate.

[0028] The present invention (14) resides in the material film production apparatus of invention 13, characterized in that the electric potential body comprises electroconductive wires in a lattice pattern.

[0029] The present invention (15) resides in a material film production apparatus comprising:

a vacuum vessel;

magnetic field generation means;

plasma generation means for generating plasma including encapsulation target ions;

collision ion generation means for generating collision ions;

a deposition-assistance substrate for depositing a material film thereon; and

a bias power supply configured to apply a bias voltage to the deposition-assistance substrate.

[0030] The present invention (16) resides in a material film production apparatus comprising:

a vacuum vessel;

magnetic field generation means;

plasma generation means for generating plasma including collision ions;

a deposition-assistance substrate for depositing a material film thereon;

encapsulation target molecule shooting means for shooting vapor including encapsulation target molecules to

the deposition-assistance substrate; and

a bias power supply configured to apply a bias voltage to the deposition-assistance substrate.

Effect of the Invention

[0031]

1. The electric potential body is arranged in the plasma to be irradiated to the material film, and the voltage to be applied to the electric potential body is controlled, thereby enabling a density of ions in the plasma to be controlled and controllability of the material film production process to be improved.

2. The electric potential body arranged in the plasma comprises electroconductive wires in the lattice pattern, thereby enabling a density of ions to be controlled to become uniform within a cross section of a plasma flow without disturbing the plasma flow by the electric potential body.

3. By measuring an electric current flowing between the deposition-assistance substrate and the bias power supply, it becomes possible to accurately measure a density of ions to be irradiated to the deposition-assistance substrate.

4. Since it is possible to produce fullerenes such as encapsulating-fullerene, hetero-fullerene, and the like at a good efficiency, it becomes possible to attain mass-production of fullerenes for industrial utilization.

5. By simultaneously irradiating encapsulation target ions and collision ions, or encapsulation target molecules and collision ions toward material molecules constituting a material film, the material molecules are largely deformed to thereby increase a probability of encapsulation of the encapsulation target ions or encapsulation target molecules into the material molecules, respectively.

6. Plasma is transported by utilizing the magnetic field, thereby enabling charged particles having a polarity opposite to that of irradiating ions, to be transported together with the irradiating ions. Thus, attractive forces act between the charged particles constituting the plasma in a manner to rarely diverge the plasma, thereby enabling achievement of a high density ion irradiation even with a low energy.

7. By the method for simultaneously irradiating collision ions, it becomes possible to improve a production efficiency of fullerene encapsulate an atom such as K, Rb, N, F, or the like which has been conventionally difficult in encapsulation due to a larger ion diameter. For fullerenes which have been conventionally possible and each encapsulate an atom such as Li, Na, or the like, it becomes possible to further improve a production efficiency thereof.

8. According to the method for simultaneously irradiating collision ions, it becomes possible to improve a production efficiency of encapsulating-nanotubes encapsulating molecules having larger diameters,

respectively.

9. The simultaneous irradiation of collision ions enables encapsulation target ions to be encapsulated even at relatively lower acceleration energies, thereby making it unnecessary to conduct ion irradiation at such higher acceleration energies which rather sputter a material film.

10. The collision ions are each made to have a diameter of 3.0Å or larger, thereby enabling a probability, that the collision ions are encapsulated in fullerene, to be decreased.

11. Fullerene positive ions or fullerene negative ions are utilized as collision ions, so that encapsulation target ions are encapsulated in part of collision ions as well, thereby further improving a production efficiency of encapsulating-fullerene.

BRIEF DESCRIPTION OF THE DRAWINGS

[0032]

[FIG. 1] A cross-sectional view of a material film production apparatus according to a first concrete example of the present invention.

[FIG. 2] A cross-sectional view of a material film production apparatus according to a second concrete example of the present invention.

[FIG. 3] A cross-sectional view of a material film production apparatus according to a third concrete example of the present invention.

[FIG. 4] A cross-sectional view of a material film production apparatus according to a fourth concrete example of the present invention.

[FIG. 5] A cross-sectional view of a material film production apparatus according to a fifth concrete example of the present invention.

[FIG. 6] A cross-sectional view of a material film production apparatus according to a sixth concrete example of the present invention.

[FIG. 7] A cross-sectional view of a material film production apparatus according to a seventh concrete example of the present invention.

[FIG. 8] A cross-sectional view of a material film production apparatus according to an eighth concrete example of the present invention.

[FIG. 9] A cross-sectional view of a material film production apparatus according to a ninth concrete example of the present invention.

[FIG. 10] An explanatory view of sizes of encapsulating-fullerene, empty fullerene, and ions.

[FIG. 11] An explanatory view of collision of encapsulation target ion and collision ion with fullerene, according to the material film production method of the present invention.

[FIG. 12] An explanatory view of collision of encapsulation target molecule and collision ion with carbon nanotube.

[FIG. 13] A cross-sectional view of a material film production apparatus according to the background art.

[FIG. 14] An explanatory view of collision of encapsulation target ion with fullerene by virtue of the material film production method according to the background art.

Explanation of reference numerals

[0033]

1, 51, 81, 111, 141, 171, 201, 231, 261, 301 vacuum vessel

2, 52, 82, 112, 142, 172, 202, 232, 262, 302 vacuum pump

3, 53, 83, 113, 116, 117, 143, 173, 203, 233, 263, 303 electromagnetic coil

4, 54, 84, 204, 234, 264, 304 heating filament

5, 55, 85, 205, 235, 265, 305 hot plate

6, 56, 86, 206, 236, 306 alkali metal sublimation oven

7, 57, 87, 207, 237, 307 alkali metal gas introduction pipe

8, 58, 88, 208, 238, 308 alkali metal ion

9, 62, 89, 120, 149, 180, 209, 239, electron

266, 309

10, 63, 90, 121, 146, 176, 210, 240, plasma flow

267, 310

11, 91, 211, 241, grid electrode

268

12, 92, 212, 242, grid voltage control power supply

269

13, 64, 98, 127, 155, 183, 218, 246, plasma prove

273, 311

14, 65, 99, 128, 156, 184, prove electric current

219, measurement device

247, 274, 312

15, 66, 93, 103, 122, 129, fullerene sublimation oven

152,

157, 185, 213, 270, 277,

313

16, 67, 104, 130, 158, 186, fullerene gas introduction

278, 314 pipe

17, 68, 95, 105, 124, 131, fullerene molecule

154,

160, 187, 215, 245, 272,

315

18, 69, 100, 132, 161, deposition-assistance substrate

188, 220,

250, 280, 316

19, 70, 101, 133, 162, 189, 221, 251, deposited film

281, 317

20, 71, 102, 134, 163, 190, 222, 252, 282, 318 bias voltage control power supply

94, 123, 153, 214, 271 re-sublimation cylinder

96, 125, 216, 249, 276 fullerene positive ion

97, 126, 159, 217, 248, 275 fullerene negative ion

59 collision atom sublimation oven

60 collision atom gas introduction pipe

61 collision ion

114 microwave transmitter

115 nitrogen gas introduction pipe

118 PMH antenna

119 nitrogen ion

144, 174 halogen gas introduction pipe

145, 175 high frequency induction coil

147, 177 positive ion

148, 178 fluorine ion

179 chlorine ion

279 encapsulation target ion

BEST MODE FOR CARRYING OUT THE INVENTION

[0034] (Control of Ion Density)

In order to precisely control a collision probability of an alkali metal ion with a fullerene molecule, it is

devised to provide a grid electrode after a plasma generating portion and to apply a bias voltage to the grid electrode, thereby controlling a density of alkali metal ions to be irradiated to a deposition-assistance substrate. The bias voltage to be applied to the grid electrode allows control of an amount of alkali metal ions which pass through the grid electrode. By controlling the density of alkali metal ions to be irradiated to fullerene molecules to be shot out of a fullerene sublimation oven at a certain density, it becomes possible to precisely control a collision probability between alkali metal ions and fullerene molecules.

[0035] Note that, in the material film production method according to the present invention, there is utilized a uniform magnetic field generated by magnetic field generation means such as an electromagnetic coil, as a method for transporting: plasma generated by plasma generation means and including irradiating ions; from the plasma generation means, to a deposition-assistance substrate where irradiating ions are irradiated into a material film. This enables transportation of charged particles of a polarity opposite to that of irradiating ions simultaneously with the irradiating ions, so that attractive forces act between the charged particles constituting the plasma, thereby rarely diverging the plasma. It is thus possible to achieve a high density ion irradiation even with a low energy.

[0036] (Material Film Production Apparatus according to Control of Ion Density)

There will be explained a best mode of a production apparatus of the present invention configured to produce a material film such as encapsulating-fullerene by controlling an ion density by a control voltage to be applied to a grid electrode, based on concrete examples.

[0037] First Concrete Example:

(Ion Irradiation Scheme)

FIG. 1 is a cross-sectional view of a material film production apparatus according to a first concrete example of the present invention. The first concrete example is a encapsulating-fullerene production apparatus configured to irradiate alkali metal ions into fullerene to thereby produce alkali-metal- encapsulating fullerene.

[0038] The production apparatus is constituted of a vacuum vessel 1, an electromagnetic coil 3, alkali metal plasma generation means, a grid electrode 11, a plasma prove 13, fullerene vapor deposition means, a deposition-assistance substrate 18, and a bias voltage control power supply 20.

[0039] The vacuum vessel 1 is evacuated to a degree of vacuum of about 10^{-4}Pa by a vacuum pump 2. The plasma generation means is constituted of a heating filament 4, a hot plate 5, an alkali metal sublimation oven 6, and an alkali metal gas introduction pipe 7. Alkali metal is heated by the sublimation oven 6, and the generated alkali

metal gas is shot from the introduction pipe 7 onto the hot plate 5, so that alkali metal atoms are ionized on the high-temperature hot plate, thereby generating alkali metal ions. Simultaneously therewith, thermoelectrons are generated from the hot plate, thereby generating plasma including alkali metal ions 8 and electrons 9. The thus generated plasma is confined in a magnetic field direction within the vacuum vessel 1 along a uniform magnetic field formed by the electromagnetic coil 3, and is established into a plasma flow 10 flowing from the hot plate 5 toward the deposition-assistance substrate 18.

[0040] The plasma flow 10 generated by the plasma generation means firstly passes through the grid electrode 11. Applied to the grid electrode 11 is a control voltage by a grid voltage control power supply 12, thereby controlling a density of alkali metal ions and a temperature of electrons in the plasma. Particular limitations are not applied to as to which of positive voltage, earth voltage, and negative voltage the control voltage value is set at, and there is adopted an optimum condition taking account of a production efficiency of encapsulating-fullerene, for example. It is also possible to make the control voltage variable and to control the voltage value based on values of an ion density, ion energy, and the like measured by the plasma prove 13, thereby optimizing a production efficiency of encapsulating-fullerene.

[0041] Applied to the deposition-assistance substrate 18, to which the plasma flow 10 is irradiated, is a negative bias voltage by the bias voltage control power supply 20. Further, simultaneously with the plasma irradiation to the deposition-assistance substrate, fullerene vapor is shot to the deposition-assistance substrate 18 by the fullerene vapor deposition means. The fullerene vapor deposition means is constituted of a fullerene sublimation oven 15 and a fullerene gas introduction pipe 16. The fullerene sublimation oven 15 heats fullerene to thereby generate a fullerene gas, which is then shot to the deposition-assistance substrate 18 from the introduction pipe 16 having a tip end directed toward the deposition-assistance substrate 18. The alkali metal ions 8 within the plasma flow are provided with acceleration energies by the negative voltage applied to the deposition-assistance substrate 18. The alkali metal ions 8 collide with fullerene molecules 17 near the deposition-assistance substrate or on the deposition-assistance substrate, and are encapsulated within the fullerene molecules 17, thereby depositing a film 19 including encapsulating-fullerene on the deposition-assistance substrate 18. It is also possible that the bias voltage to be applied to the deposition-assistance substrate 18 is made variable, and the bias voltage value is controlled based on the values measured by the plasma prove 13, thereby optimizing a production efficiency of

encapsulating-fullerene.

[0042] It is also possible to measure an alkali metal ion density, an ion irradiation amount, and the like, even by a method for arranging an ammeter between the bias voltage control power supply 20 and the deposition-assistance substrate 18, thereby measuring an electric current flowing through the deposition-assistance substrate. Further, it is possible to obtain a shooting velocity of fullerene vapor, by previously conducting vapor deposition of fullerene onto the deposition-assistance substrate so as to monitor a film thickness, and by measuring a timewise change of a thickness of a deposited film.

[0043] There can be controlled an alkali metal ion density within plasma by a voltage to be applied to the grid electrode to thereby precisely control densities of alkali metal ions and fullerene molecules, thereby allowing an improved production efficiency of encapsulating-fullerene.

[0044] The above explained method for controlling an ion density by the grid electrode can be used not only in production of encapsulating-fullerene where alkali metal acts as an encapsulation target atom but also in production of encapsulating-fullerene which encapsulates another atom such as nitrogen, halogen, hydrogen, inert element, alkaline earth metal, or the like, in a manner to obtain the same effect as the production of alkali-metal-encapsulating fullerene.

[0045] Note that, without limited to the production of encapsulating-fullerene, it is also possible to optimize a production efficiency of a material film by arranging a grid electrode having a control voltage applied thereto after a plasma generating portion to thereby control an ion density within plasma, for: a encapsulating-nanotube comprising a nanotube encapsulating an atom or molecule; hetero-fullerene to be obtained by irradiating an ion(s) comprising a substitutional atom(s) toward fullerene so as to substitute carbon atoms constituting the fullerene by the substitutional atom(s); chemically modified fullerene to be obtained by irradiating ions of modification atoms or molecules, thereby adding a modifying group(s) to the fullerene; and the like.

[0046] (Irradiation of Collision Ion)

To improve a production efficiency of encapsulating-fullerene encapsulating a relatively large atom such as K, it is devised that, upon irradiation of encapsulation target atom ions (encapsulation target ions) into fullerene, the fullerene is caused to be irradiated with ions (collision ions) of atoms (collision atoms) each having the same polarity as an encapsulation target ion and each having a diameter and a mass larger than those of the encapsulation target ion. Although the collision ions are each large in diameter and are thus encapsulated in fullerene at an extremely low probability, the collision ions have larger masses and thus are capable of giving

sufficiently large energies to fullerene upon collision therewith, thereby increasing deformation of the fullerene. This largely opens six-membered rings of the fullerene, so that the encapsulation target ions, which have been irradiated simultaneously with the collision ions and which are smaller than the encapsulation target ions, can be easily incorporated into the fullerene.

[0047] (Irradiating Ion, Encapsulation Target Ion, and Collision Ion)

There will be explained terms related to ions according to the material film production method of the present invention.

The term "irradiating ion" refers to an ion (charged particle) in a case that the ion is to be irradiated into a material film or material molecule by an ion irradiation scheme or plasma irradiation scheme. Examples of irradiating ions include atoms and molecules each having a positive electric charge or negative electric charge. As a result of conduction of ion irradiation, there may be caused a physical or chemical change in a material film or material molecule, including situations where irradiating ions enter between molecules constituting a material film, as impurities, where irradiating ions bond to a material molecule to thereby cause chemical modification or heterogenization, and where there is caused such encapsulation that irradiating ion(s) enter the interior of a cage-like or tubular material molecule.

Those irradiating ions, which are to be encapsulated, are particularly called "encapsulation target ions", respectively. Those irradiating ions, which collide with a material molecule and which are not encapsulated therein, are particularly called "collision ions", respectively.

[0048] (Sizes of Fullerene and Ions)

The term "fullerene" used herein refers to a hollow carbon cluster substance represented by C_n (n=60, 70, 76, 78, 82, 84,…), and examples thereof include C_{60}, C_{70}, and the like. Further, the term "fullerene" shall also be applied to those carbon cluster substances including: a repetitive bonded body (by ionic bond, covalent bond, or the like) of the same fullerene, such as a fullerene dimer; a mixture of a plurality of different fullerenes such as C_{60} and C_{70}; and the like.

[0049] FIG. 10 is an explanatory view of sizes of encapsulating-fullerene, empty fullerene, and encapsulation target atom ions. Shown as fullerene is C_{60} which is a representative carbon cluster molecule, and so are alkali metals, nitrogen, and halogens which are representative ones of encapsulation target atoms. As shown in this figure, C_{60} has six-membered rings having an averaged diameter of 2.48Å.

[0050] Concerning combinations of encapsulation target ions and collision ions, it is desirable to employ a positive ion such as that of Cs, Fr, or the like as a collision ion, in case that an encapsulation target ion is

a positive ion such as that of Li, Na, K, N, or the like. Further, it is desirable to employ a negative ion such as that of Cl, Br, I, or the like, in case that an encapsulation target ion is a negative ion such as that of F. Equalizing an ion polarity of a an encapsulation target ion with that of a collision ion, enables simultaneous provision of acceleration energies to the encapsulation target ion and collision ion by a bias voltage to be applied to a deposition-assistance substrate.

[0051] It is required for a collision ion to be in such a size which causes a sufficiently large deformation of a molecule constituting a material film, and which is scarcely encapsulated in the molecule. It is desirable for a collision ion to have an ion diameter of 3.0Å or larger, since six-membered rings of C_{60} have an averaged diameter of 2.48Å.

[0052] Further, as a collision ion, it is possible to use not only an atomic ion to be provided by ionizing an applicable atom, but also a molecular ion to be provided by ionizing an applicable molecule such as a fullerene molecule. Fullerene molecules each have a larger electron affinity and a relatively small ionization energy. As such, it is possible to selectably ionize a fullerene molecule into a positive ion or negative ion, by controlling an energy of an electron upon colliding the electron with the fullerene molecule so as to ionize it. Concretely, it is possible to form a negative fullerene ion by collision of

an electron having an energy less than 10eV, and to form a positive fullerene ion by collision of an electron having an energy of 10eV or higher.

[0053] As understood from the data of ion diameters, in case of those ions of Li, Na, and the like which are smaller than the averaged diameter of 2.48Å of six-membered rings of fullerene, it is possible to form encapsulating-fullerene at a higher efficiency even without adopting collision ions. However, in case of relatively large ions such as those of K, N, F, and the like, it becomes possible to drastically improve a formation efficiency of encapsulating-fullerene, only by irradiating collision ions to a fullerene film simultaneously with irradiation of encapsulation target ions thereto. Further, even in case of relatively small ions such as those of Li, Na, or the like, it is rather possible to further improve a formation efficiency of encapsulating-fullerene, by irradiating collision ions to a fullerene film simultaneously with irradiation of encapsulation target ions thereto.

[0054] (Ion Irradiation into Fullerene)

FIG. 11(a) through FIG. 11(c) are explanatory views of collision of an encapsulation target ion and a collision ion with fullerene, according to the material film production method of the present invention. In FIG. 11(a), collided with a C_{60} molecule formed on a deposition-assistance substrate, is a positive ion of C_{60} acting as a

collision ion. At a moment of collision, the C_{60} molecule and the positive ion of C_{60} are largely deformed. Further, a positive ion of K collides with the C_{60} molecule (FIG. 11(b)). Since the C_{60} molecule has been largely deformed, its openings have each been enlarged, so that the positive ion of K easily enters the cage of C_{60} molecule, thereby forming K-encapsulating C_{60} (FIG. 11(c)).

[0055] (Ion Irradiation into Carbon Nanotube)

FIG. 12(a) through FIG. 12(c) are explanatory views of collision of an encapsulation target molecule and a collision ion with a carbon nanotube, according to the material film production method of the present invention. In FIG. 12(a), collided with the carbon nanotube formed on a deposition-assistance substrate, is a positive ion of C_{60} acting as a collision ion. At a moment of collision, the carbon nanotube and the positive ion of C_{60} are largely deformed. Further, TTF as an encapsulation target molecule collides with the carbon nanotube (FIG. 12(b)). Since the carbon nanotube has been largely deformed, its openings have each been enlarged, so that the TTF easily enters the cage of carbon nanotube, thereby forming TTF- encapsulating carbon nanotube (FIG. 12(c)).

[0056] (Material Film Production Apparatus according to Irradiation of Collision Ions)

There will be explained a best mode of a production apparatus of the present invention configured to produce a material film such as encapsulating-fullerene by

simultaneously irradiating encapsulation target ions and collision ions to a deposition-assistance substrate, based on concrete examples.

[0057] Second Concrete Example:

FIG. 2 is a cross-sectional view of a material film production apparatus according to a second concrete example of the present invention. The second concrete example is an encapsulating-fullerene production apparatus configured to irradiate alkali metal ions and collision ions to fullerene to thereby produce alkali-metal- encapsulating fullerene. Usable as alkali metal is Li, Na, K, or the like. Usable as collision ion is that of Cs, Fr, or the like.

[0058] The production apparatus is constituted of a vacuum vessel 51, an electromagnetic coil 53, alkali metal plasma generation means, a plasma prove 64, fullerene vapor deposition means, a deposition-assistance substrate 69, and a bias voltage control power supply 71.

[0059] The vacuum vessel 51 is evacuated to a degree of vacuum of about 10^{-4}Pa by a vacuum pump 52. The plasma generation means is constituted of a heating filament 54, a hot plate 55, an alkali metal sublimation oven 56, an alkali metal gas introduction pipe 57, a collision atom sublimation oven 59, and a collision atom gas introduction pipe 60. Alkali metal is heated by the sublimation oven 56, and the generated alkali metal gas is shot from the introduction pipe 57 onto the hot plate 55. Simultaneously

therewith, a collision atom gas generated by the sublimation oven 59 is shot from the introduction pipe 60 onto the hot plate 55, so that alkali metal atoms and collision atoms are ionized by contact ionization, thereby generating plasma including alkali metal ions, collision ions, and electrons. The thus generated plasma is confined in a magnetic field direction within the vacuum vessel 51 along a uniform magnetic field formed by the electromagnetic coil 53, and is established into a plasma flow 63 flowing from the hot plate 55 toward the deposition-assistance substrate 69.

[0060] Simultaneously with the plasma irradiation to the deposition-assistance substrate 69, the fullerene vapor deposition means shoots fullerene vapor toward the deposition-assistance substrate 69. The fullerene vapor deposition means is constituted of a fullerene sublimation oven 66 and a fullerene gas introduction pipe 67. Applied to the deposition-assistance substrate 69 is a negative bias voltage by the bias voltage control power supply 71. By virtue of the function of the bias voltage, alkali metal ions and collision ions acting as positive ions in plasma are provided with acceleration energies near the deposition-assistance substrate 69, and collide with fullerene molecules near the deposition-assistance substrate or on the deposition-assistance substrate. Since collision ions having larger masses collide with fullerene molecules, the fullerene molecules are largely deformed and

six-membered rings of the fullerene molecules are largely opened. As such, alkali metal ions colliding with fullerene molecules easily enter cages of the fullerene molecules, thereby increasing a formation efficiency of encapsulating-fullerene. After collision, collision ions having larger ion diameters are not encapsulated in fullerene molecules, and exhausted by the vacuum pump 52.

[0061] The plasma prove 64 is arranged in the plasma flow 63, to measure ion densities, ion energies, and the like of plasma. It is also possible that the bias voltage to be applied to the deposition-assistance substrate 69 is made variable, and the bias voltage value is controlled based on the values measured by the plasma prove 64, thereby optimizing a production efficiency of encapsulating-fullerene.

[0062] Third Concrete Example:

FIG. 3 is a cross-sectional view of a material film production apparatus according to a third concrete example of the present invention. The third concrete example is an encapsulating-fullerene production apparatus configured to irradiate collision ions including alkali metal ions and C_{60}^+ to fullerene to thereby produce alkali-metal-encapsulating fullerene. Usable as alkali metal ion is Li^+, Na^+, K^+, or the like.

[0063] The production apparatus is constituted of a vacuum vessel 81, an electromagnetic coil 83, alkali metal plasma generation means, a grid electrode 91, fullerene ion

generation means, a plasma prove 98, fullerene vapor deposition means, a deposition-assistance substrate 100, and a bias voltage control power supply 102.

[0064] The vacuum vessel 81 is evacuated to a degree of vacuum of about 10^{-4}Pa by a vacuum pump 82. The plasma generation means is constituted of a heating filament 84, a hot plate 85, an alkali metal sublimation oven 86, and an alkali metal gas introduction pipe 87. The sublimation oven 86 generates an alkali metal gas which is shot from the introduction pipe 87 onto the hot plate 85, so that alkali metal atoms are ionized on the high-temperature hot plate and established into plasma including alkali metal ions and electrons. The thus generated plasma is confined in a magnetic field direction within the vacuum vessel 81 along a uniform magnetic field formed by the electromagnetic coil 83, and is established into a plasma flow 90 flowing from the hot plate 85 toward the deposition-assistance substrate 100.

[0065] The plasma flow 90 generated by the plasma generation means firstly passes through the grid electrode 91. Applied to the grid electrode 91 is a control voltage by a grid voltage control power supply 92, thereby controlling a density of alkali metal ions and a temperature of electrons in the plasma. The control voltage is preferably a positive voltage. More preferably, the control voltage is 10V or higher. Setting the control voltage to be a positive voltage enables a temperature of

electrons in plasma to be raised. It is also possible to make the control voltage variable and to control the value of voltage to be applied to the grid electrode 91 based on a value of electron temperature measured by the plasma prove 98, thereby optimizing a production efficiency of encapsulating-fullerene.

[0066] The fullerene ion generation means for generating fullerene ions into plasma is arranged downstream of the grid electrode 91. The fullerene ion generation means is constituted of a fullerene sublimation oven 93 and a re-sublimation cylinder 94. Introduced from the fullerene sublimation oven 93 into plasma are fullerene molecules 95 which are then affected by electrons in the plasma and ionized by them, thereby generating fullerene positive ions 96 and fullerene negative ions 97. At this time, electrons in plasma have been raised in electron temperature by an action of the grid electrode 91, thereby increasing a generation probability of fullerene positive ions. Particularly, the generation probability of fullerene positive ions can be increased by causing a voltage of 10V or higher to be applied to the grid electrode 91. As a result, the plasma flow 90 is established into plasma including positive ions of alkali metal, fullerene positive ions, fullerene negative ions, and electrons.

[0067] Simultaneously with plasma irradiation to the deposition-assistance substrate 100, the fullerene vapor

deposition means shoots fullerene vapor to the deposition-assistance substrate 100. The fullerene vapor deposition means is constituted of a fullerene sublimation oven 103 and a fullerene gas introduction pipe 104. The bias voltage control power supply 102 applies a negative bias voltage to the deposition-assistance substrate 100. By virtue of the action of the bias voltage, alkali metal ions as positive ions in plasma and collision ions comprising fullerene positive ions are provided with acceleration energies near the deposition-assistance substrate 100, and collide with fullerene molecules near the deposition-assistance substrate or on the deposition-assistance substrate. Since collision ions having larger masses collide with fullerene molecules, the fullerene molecules are largely deformed and six-membered rings of the fullerene molecules are largely opened. As such, alkali metal ions colliding with fullerene molecules easily enter cages of the fullerene molecules, thereby increasing a formation efficiency of encapsulating-fullerene.

[0068] It is possible to measure ion densities, ion energies, and the like of plasma by the plasma prove 97. It is also possible that the bias voltage to be applied to the deposition-assistance substrate 100 is made variable, and the bias voltage value is controlled based on the values measured by the plasma prove 97, thereby optimizing a production efficiency of encapsulating-fullerene.

[0069] Fourth Concrete Example:

FIG. 4 is a cross-sectional view of a material film production apparatus according to a fourth concrete example of the present invention. The fourth concrete example of the present invention is an encapsulating-fullerene production apparatus configured to irradiate collision ions comprising nitrogen ions and C_{60}^{+} to fullerene to thereby produce nitrogen- encapsulating fullerene.

[0070] The production apparatus is constituted of a vacuum vessel 111, an electromagnetic coil 113, nitrogen plasma generation means, fullerene ion generation means, a plasma prove 127, fullerene vapor deposition means, a deposition-assistance substrate 132, and a bias voltage control power supply 134.

[0071] The vacuum vessel 111 is evacuated to a degree of vacuum of about 10^{-4}Pa by a vacuum pump 112. The nitrogen plasma generation means is constituted of a plasma generation chamber, a nitrogen gas introduction pipe 115, a microwave transmitter 114, electromagnetic coils 116, 117, and a PMH antenna 118. Nitrogen gas is introduced from the nitrogen gas introduction pipe 115 into the plasma generation chamber, and atoms, molecules, and the like constituting the nitrogen gas are excited by the microwave transmitter 114 to thereby generate nitrogen plasma. The electromagnetic coils 116, 117 exemplarily comprise ones in circular shape for surrounding the plasma generation chamber and arranged in a mutually separated state, and electric currents are caused to flow through the

electromagnetic coils in the same direction. There are formed strong magnetic fields near the electromagnetic coils 116, 117, respectively, and there is formed a weak magnetic field in an area inbetween the electromagnetic coils 116, 117. Since rebound of ions, electrons, and the like is caused at the strong magnetic fields, there is formed plasma temporarily confined and having a higher energy.

[0072] The PMH antenna 118 is provided for supplying a high-frequency power (13.56MHz, MAX 2kW) by changing phases of multiple coil elements, thereby resultingly causing a larger electric field difference between the coil elements. This causes the plasma generated within the plasma generation chamber, to become highly dense over the entire region. By constituting the plasma generation means in the above manner, it becomes possible to effectively generate plasma including numerous N^+ ions each comprising one nitrogen atom and particularly having a higher excitation energy.

[0073] The thus generated plasma is confined in a magnetic field direction in the vacuum vessel 111 along a uniform magnetic field (B=2 to 7kG) formed by the electromagnetic coil 113, and is established into a plasma flow 121 flowing from the plasma generation chamber toward the deposition-assistance substrate 132.

[0074] The fullerene ion generation means for generating fullerene ions in plasma is arranged downstream

of the plasma generation means. The fullerene ion generation means is constituted of a fullerene sublimation oven 122 and a re-sublimation cylinder 123. Introduced from the fullerene sublimation oven 122 into plasma are fullerene molecules 124 which are then affected by electrons in the plasma and ionized by them, thereby generating fullerene positive ions 125 and fullerene negative ions 126. Since the electron temperature in the plasma is high, the generation probability of fullerene positive ions 125 is large. The plasma flow is established into plasma including positive ions of nitrogen, fullerene positive ions, fullerene negative ions, and electrons.

[0075] Simultaneously with plasma irradiation to the deposition-assistance substrate 132, the fullerene vapor deposition means shoots fullerene vapor to the deposition-assistance substrate 132. The fullerene vapor deposition means is constituted of a fullerene sublimation oven 129 and a fullerene gas introduction pipe 130. The bias voltage control power supply 134 applies a negative bias voltage to the deposition-assistance substrate 132. By virtue of the action of the bias voltage, nitrogen ions as positive ions in plasma and collision ions comprising fullerene positive ions are provided with acceleration energies near the deposition-assistance substrate 132, and collide with fullerene molecules near the deposition-assistance substrate or on the deposition-assistance substrate. Since collision ions having larger masses

collide with fullerene molecules, the fullerene molecules are largely deformed and six-membered rings of the fullerene molecules are largely opened. As such, nitrogen ions colliding with fullerene molecules easily enter cages of the fullerene molecules, thereby increasing a formation efficiency of encapsulating-fullerene.

[0076] It is possible to measure ion densities, ion energies, and the like of plasma by the plasma prove 127. It is also possible that the bias voltage to be applied to the deposition-assistance substrate 132 is made variable, and the bias voltage value is controlled based on the values measured by the plasma prove 127, thereby optimizing a production efficiency of encapsulating-fullerene.

[0077] Fifth Concrete Example:

FIG. 5 is a cross-sectional view of a material film production apparatus according to a sixth embodiment of the present invention. The sixth embodiment is an encapsulating-fullerene production apparatus configured to irradiate fluorine ions and collision ions comprising C_{60}^{+} into fullerene to thereby produce fluorine- encapsulating fullerene.

[0078] The production apparatus is constituted of a vacuum vessel 141, an electromagnetic coil 143, fluorine plasma generation means, fullerene ion generation means, a plasma prove 155, fullerene vapor deposition means, a deposition-assistance substrate 161, and a bias voltage control power supply 163.

[0079] The vacuum vessel 141 is evacuated to a degree of vacuum of about 10^{-4}Pa by a vacuum pump 112. The fluorine plasma generation means is constituted of a plasma generation chamber, a source gas introduction pipe 144, and a high frequency induction coil 145. Introduced from the source gas introduction pipe 144 into the plasma generation chamber is a source gas such as CF_4, and there is flowed an alternating current through the high frequency induction coil 145 arranged around the plasma generation means to thereby excite particles constituting the source gas, thereby generating plasma including ions such as CF_3^+, F^-, and electrons. Included in the plasma are ions 147 such as CF_3^+, in addition to fluorine ions 148 required for production of encapsulating-fullerene. The thus generated plasma is confined in a magnetic field direction in the vacuum vessel 141 along a uniform magnetic field (B=2 to 7kG) formed by the electromagnetic coil 143, and is established into a plasma flow flowing from the plasma generation portion toward the deposition-assistance substrate 162.

[0080] The fullerene ion generation means for generating fullerene ions in plasma is arranged downstream of the plasma generation means. The fullerene ion generation means is constituted of a fullerene sublimation oven 152 and a re-sublimation cylinder 153. Introduced from the fullerene sublimation oven 152 into plasma are fullerene molecules 154 which are then affected by

electrons in the plasma and ionized by them, thereby generating fullerene positive ions and fullerene negative ions 159.

[0081] Simultaneously with plasma irradiation to the deposition-assistance substrate 161, the fullerene vapor deposition means shoots fullerene vapor to the deposition-assistance substrate 161. The fullerene vapor deposition means is constituted of a fullerene sublimation oven 157 and a fullerene gas introduction pipe 158. The bias voltage control power supply 163 applies a positive bias voltage to the deposition-assistance substrate 161. By virtue of the action of the bias voltage, fluorine ions as negative ions in plasma and collision ions comprising fullerene negative ions are provided with acceleration energies near the deposition-assistance substrate 161, and collide with fullerene molecules near the deposition-assistance substrate or on the deposition-assistance substrate. Meanwhile, positive ions such as CF_3^+ unrequired for production of encapsulating-fullerene are subjected to repulsive forces by the positive bias voltage, so that the positive ions are not irradiated to the deposition-assistance substrate. Since collision ions having larger masses collide with fullerene molecules, the fullerene molecules are largely deformed and six-membered rings of the fullerene molecules are largely opened. As such, fluorine ions colliding with fullerene molecules easily enter cages of the fullerene molecules, thereby increasing

a formation efficiency of encapsulating-fullerene.

[0082] It is possible to measure ion densities, ion energies, and the like of plasma by the plasma prove 155. It is also possible that the bias voltage to be applied to the deposition-assistance substrate 161 is made variable, and the bias voltage value is controlled based on the values measured by the plasma prove 155, thereby optimizing a production efficiency of encapsulating-fullerene.

[0083] Sixth Concrete Example:

FIG. 6 is a cross-sectional view of a material film production apparatus according to a seventh embodiment of the present invention. The seventh embodiment is an encapsulating-fullerene production apparatus configured to irradiate fluorine ions and collision ions comprising chlorine ions into fullerene to thereby produce fluorine-encapsulating fullerene.

[0084] The production apparatus is constituted of a vacuum vessel 171, an electromagnetic coil 173, fluorine/chlorine plasma generation means, a plasma prove 183, fullerene vapor deposition means, a deposition-assistance substrate 188, and a bias voltage control power supply 190.

[0085] The vacuum vessel 171 is evacuated to a degree of vacuum of about 10^{-4}Pa by a vacuum pump 172. The fluorine/chlorine plasma generation means is constituted of a plasma generation chamber, a source gas introduction pipe 174, and a high frequency induction coil 175. Introduced

from the source gas introduction pipe 174 into the plasma generation chamber is a source gas such as $CFCl_3$, and there is flowed an alternating current through the high frequency induction coil 175 arranged around the plasma generation means to thereby excite particles constituting the source gas, thereby generating plasma including ions such as CF_3^+, Cl^-, F^-, and electrons. Included in the plasma are unnecessary ions 177 such as CF_3^+, in addition to fluorine ions 178 and chlorine ions 179 acting as collision ions required for production of encapsulating-fullerene. The thus generated plasma is confined in a magnetic field direction in the vacuum vessel 171 along a uniform magnetic field (B=2 to 7kG) formed by the electromagnetic coil 173, and is established into a plasma flow flowing from the plasma generation portion toward the deposition-assistance substrate 188.

[0086] Simultaneously with plasma irradiation to the deposition-assistance substrate 188, the fullerene vapor deposition means shoots fullerene vapor to the deposition-assistance substrate 188. The fullerene vapor deposition means is constituted of a fullerene sublimation oven 185 and a fullerene gas introduction pipe 186. The bias voltage control power supply 190 applies a positive bias voltage to the deposition-assistance substrate 188. By virtue of the action of the bias voltage, fluorine ions as negative ions in plasma and collision ions comprising chlorine ions are provided with acceleration energies near

the deposition-assistance substrate 188, and collide with fullerene molecules near the deposition-assistance substrate or on the deposition-assistance substrate. Meanwhile, positive ions such as CF_3^+ unrequired for production of encapsulating-fullerene are subjected to repulsive forces by the positive bias voltage, so that the positive ions are not irradiated to the deposition-assistance substrate. Since collision ions having larger masses collide with fullerene molecules, the fullerene molecules are largely deformed and six-membered rings of the fullerene molecules are largely opened. As such, fluorine ions colliding with fullerene molecules easily enter cages of the fullerene molecules, thereby increasing a formation efficiency of encapsulating-fullerene.

[0087] It is possible to measure ion densities, ion energies, and the like of plasma by the plasma prove 183. It is also possible that the bias voltage to be applied to the deposition-assistance substrate 188 is made variable, and the bias voltage value is controlled based on the values measured by the plasma prove 183, thereby optimizing a production efficiency of encapsulating-fullerene.

[0088] Seventh Concrete Example:

FIG. 7 is a cross-sectional view of a material film production apparatus according to a seventh concrete example of the present invention. The seventh concrete example is an encapsulating-fullerene production apparatus configured to irradiate alkali metal ions and collision

ions comprising C_{60}^{+} onto a fullerene film on a deposition-assistance substrate to thereby produce alkali-metal-encapsulating fullerene. Usable as alkali metal is Li, Na, K, or the like.

[0089] The production apparatus is constituted of a vacuum vessel 201, an electromagnetic coil 203, alkali metal plasma generation means, a grid electrode 211, fullerene ion generation means, a plasma prove 218, a deposition-assistance substrate 220, and a bias voltage control power supply 222.

[0090] The vacuum vessel 201 is evacuated to a degree of vacuum of about 10^{-4}Pa by a vacuum pump 202. The plasma generation means is constituted of a heating filament 204, a hot plate 205, an alkali metal sublimation oven 206, and an alkali metal gas introduction pipe 207. The sublimation oven 206 generates an alkali metal gas which is shot from the introduction pipe 207 onto the hot plate 205, so that alkali metal atoms are ionized on the high-temperature hot plate and established into plasma including alkali metal ions and electrons. The thus generated plasma is confined in a magnetic field direction within the vacuum vessel 201 along a uniform magnetic field formed by the electromagnetic coil 203, and is established into a plasma flow 210 flowing from the hot plate 205 toward the deposition-assistance substrate 220.

[0091] The plasma flow 210 generated by the plasma generation means firstly passes through the grid electrode

211. Applied to the grid electrode 211 is a control voltage by a grid voltage control power supply 212, thereby controlling a density of alkali metal ions and a temperature of electrons in the plasma. The control voltage is preferably a positive voltage. More preferably, the control voltage is 10V or higher. Setting the control voltage to be a positive voltage enables a temperature of electrons in plasma to be raised. It is also possible to make the control voltage variable and to control the value of voltage to be applied to the grid electrode 211 based on a value of electron temperature measured by the plasma prove 218, thereby optimizing a production efficiency of encapsulating-fullerene.

[0092] The fullerene ion generation means for generating fullerene ions into plasma is arranged downstream of the grid electrode 211. The fullerene ion generation means is constituted of a fullerene sublimation oven 213 and a re-sublimation cylinder 214. Introduced from the fullerene sublimation oven 213 into plasma are fullerene molecules 215 which are then affected by electrons in the plasma and ionized by them, thereby generating fullerene positive ions 216 and fullerene negative ions 217. At this time, electrons in plasma have been raised in electron temperature by an action of the grid electrode 211, thereby increasing a generation probability of fullerene positive ions. Particularly, the generation probability of fullerene positive ions can be

increased by causing a voltage of 10V or higher to be applied to the grid electrode 211. As a result, the plasma flow 210 is established into plasma including positive ions of alkali metal, fullerene positive ions, fullerene negative ions, and electrons.

[0093] Previously placed on the deposition-assistance substrate 220 is a deposited film 221 such as C_{60}, deposited by a vapor deposition method, for example. The bias voltage control power supply 222 applies a negative bias voltage to the deposition-assistance substrate 220. By virtue of the action of the bias voltage, alkali metal ions as positive ions in plasma and collision ions comprising fullerene positive ions are provided with acceleration energies near the deposition-assistance substrate 220, and collide with fullerene molecules constituting the deposited film on the deposition-assistance substrate. Since collision ions having larger masses collide with fullerene molecules, the fullerene molecules are largely deformed and six-membered rings of the fullerene molecules are largely opened. As such, alkali metal ions colliding with fullerene molecules easily enter cages of the fullerene molecules, thereby increasing a formation efficiency of encapsulating-fullerene.

[0094] It is possible to measure ion densities, ion energies, and the like of plasma by the plasma prove 218. It is also possible that the bias voltage to be applied to the deposition-assistance substrate 220 is made variable,

and the bias voltage value is controlled based on the values measured by the plasma prove 218, thereby optimizing a production efficiency of encapsulating-fullerene.

[0095] Although the seventh concrete example has been described for a situation where positive ions acting as encapsulation target atoms and collision ions comprising fullerene positive ions are simultaneously irradiated to the deposited film comprising fullerene on the deposition-assistance substrate, there can be obtained an effect of improving a production efficiency of encapsulating-fullerene even in case of adopting positive ions such as those of Cs or Fr as collision ions instead of fullerene positive ions. Further, in case that encapsulation target atoms to be irradiated to a deposited film are negative ions, there can be adopted negative collision ions to thereby obtain the same effect of improving a production efficiency of encapsulating-fullerene as the case where encapsulation target atoms comprises positive ions.

[0096] Eighth Concrete Example:

FIG. 8 is a cross-sectional view of a material film production apparatus according to an eighth concrete example of the present invention. The eighth concrete example is an encapsulating-carbon nanotube production apparatus configured to irradiate alkali metal ions and collision ions comprising C_{60}^{+} to a carbon nanotube film on a deposition-assistance substrate to thereby produce an alkali metal- encapsulating carbon nanotube. Usable as

alkali metal is Li, Na, K, Cs, Fr, or the like.

[0097] The production apparatus is constituted of a vacuum vessel 231, an electromagnetic coil 233, alkali metal plasma generation means, a grid electrode 241, fullerene ion generation means, a plasma prove 246, a deposition-assistance substrate 250, and a bias voltage control power supply 252.

[0098] The vacuum vessel 231 is evacuated to a degree of vacuum of about 10^{-4}Pa by a vacuum pump 232. The plasma generation means is constituted of a heating filament 234, a hot plate 235, an alkali metal sublimation oven 236, and an alkali metal gas introduction pipe 237. The sublimation oven 236 generates an alkali metal gas which is shot from the introduction pipe 237 onto the hot plate 235, so that alkali metal atoms are ionized on the high-temperature hot plate and established into plasma including alkali metal ions and electrons. The thus generated plasma is confined in a magnetic field direction within the vacuum vessel 231 along a uniform magnetic field formed by the electromagnetic coil 233, and is established into a plasma flow 240 flowing from the hot plate 235 toward the deposition-assistance substrate 250.

[0099] The plasma flow 240 generated by the plasma generation means firstly passes through the grid electrode 241. Applied to the grid electrode 241 is a control voltage by a grid voltage control power supply 242, thereby controlling a density of alkali metal ions and a

temperature of electrons in the plasma. The control voltage is preferably a positive voltage. More preferably, the control voltage is 10V or higher. Setting the control voltage to be a positive voltage enables a temperature of electrons in plasma to be raised. It is also possible to make the control voltage variable and to control the value of voltage to be applied to the grid electrode 241 based on a value of electron temperature measured by the plasma prove 246, thereby optimizing a production efficiency of encapsulating-carbon nanotube.

[0100] The fullerene ion generation means for generating fullerene ions into plasma is arranged downstream of the grid electrode 241. The fullerene ion generation means is constituted of a fullerene sublimation oven 243 and a re-sublimation cylinder 244. Introduced from the fullerene sublimation oven 243 into plasma are fullerene molecules 245 which are then affected by electrons in the plasma and ionized by them, thereby generating fullerene positive ions 249 and fullerene negative ions 248. At this time, electrons in plasma have been raised in electron temperature by an action of the grid electrode 241, thereby increasing a generation probability of fullerene positive ions. Particularly, the generation probability of fullerene positive ions can be increased by causing a voltage of 10V or higher to be applied to the grid electrode 241. As a result, the plasma flow 240 is established into plasma including positive ions

of alkali metal, fullerene positive ions, fullerene negative ions, and electrons.

[0101] Previously placed on the deposition-assistance substrate 250 is a carbon nanotube film 251 deposited by a method such as vapor deposition method, laser vaporization method, arc discharge method, or the like. The bias voltage control power supply 252 applies a negative bias voltage to the deposition-assistance substrate 250. By virtue of the action of the bias voltage, alkali metal ions as positive ions in plasma and collision ions comprising fullerene positive ions are provided with acceleration energies near the deposition-assistance substrate 250, and collide with carbon nanotubes on the deposition-assistance substrate. Since collision ions having larger masses collide with carbon nanotubes, the carbon nanotubes are largely deformed and six-membered rings constituting the carbon nanotubes are largely opened. As such, alkali metal ions colliding with carbon nanotubes easily enter tubular bodies of the carbon nanotubes, thereby increasing a formation efficiency of encapsulating-carbon nanotubes.

[0102] It is possible to measure ion densities, ion energies, and the like of plasma by the plasma prove 246. It is also possible that the bias voltage to be applied to the deposition-assistance substrate 250 is made variable, and the bias voltage value is controlled based on the values measured by the plasma prove 246, thereby optimizing a production efficiency of encapsulating-carbon nanotubes.

[0103] The material film production method of the present invention is not limited to carbon nanotube, and can be applied to situations where an encapsulation target substance is to be encapsulated in another nanotube such as BN nanotube, and where atom(s), molecule(s), or the like as an encapsulation target substance(s) other than alkali metals is/are to be encapsulated in nanotubes. As collision ions, it is possible to adopt: positive ions such as those of Cs, Fr, or the like without limited to fullerene positive ions when encapsulation target ions are positive ones; and negative ions such as fullerene negative ions, those of Cl, Br, I, or the like when encapsulation target ions are negative ones.

[0104] Ninth Concrete Example:

The present invention is applicable not only to a material film production method where ionizable atom(s), molecule(s), or the like is/are to be encapsulated in a material film, but also to a molecule-containing material production method configured to encapsulate molecule(s), which are hardly ionized, into a material film. FIG. 9 is a cross-sectional view of a material film production apparatus according to a ninth concrete example of the present invention. The ninth concrete example is an encapsulating-carbon nanotube production apparatus configured to irradiate collision ions comprising C_{60}^{+} to a carbon nanotube film on a deposition-assistance substrate and to simultaneously irradiate vapor comprising TTF

molecules to the carbon nanotube film, thereby producing TTF- encapsulating carbon nanotubes.

[0105] The production apparatus is constituted of a vacuum vessel 261, an electromagnetic coil 263, electron plasma generation means, a grid electrode 268, fullerene ion generation means, a plasma prove 273, TTF vapor deposition means, a deposition-assistance substrate 280, and a bias voltage control power supply 282.

[0106] The vacuum vessel 261 is evacuated to a degree of vacuum of about 10^{-4}Pa by a vacuum pump 262. The electron plasma generation means is constituted of a heating filament 264 and a hot plate 265. The hot plate 265 is heated by the heating filament 264 within the vacuum vessel to generate plasma comprising thermoelectrons, such that the thus generated plasma is confined in a magnetic field direction within the vacuum vessel 261 along a uniform magnetic field formed by the electromagnetic coil 263, and is established into a plasma flow 267 flowing from the hot plate 265 toward the deposition-assistance substrate 280.

[0107] The plasma flow 267 generated by the electron plasma generation means firstly passes through the grid electrode 268. Applied to the grid electrode 268 is a control voltage by a grid voltage control power supply 269, thereby controlling a temperature of electrons in the plasma. The control voltage is preferably a positive voltage. More preferably, the control voltage is 10V or

higher. Setting the control voltage to be a positive voltage enables a temperature of electrons in plasma to be raised. It is also possible to make the control voltage variable and to control the value of voltage to be applied to the grid electrode 268 based on a value of electron temperature measured by the plasma prove 273.

[0108] The fullerene ion generation means for generating fullerene ions into plasma is arranged downstream of the grid electrode 268. The fullerene ion generation means is constituted of a fullerene sublimation oven 270 and a re-sublimation cylinder 271. Introduced from the fullerene sublimation oven 270 into plasma are fullerene molecules 272 which are then affected by electrons in the plasma and ionized by them, thereby generating fullerene positive ions 276 and fullerene negative ions 275. At this time, electrons in plasma have been raised in electron temperature by an action of the grid electrode 268, thereby increasing a generation probability of fullerene positive ions. Particularly, the generation probability of fullerene positive ions can be increased by causing a voltage of 10V or higher to be applied to the grid electrode 268. As a result, the plasma flow 267 is established into plasma including fullerene positive ions, fullerene negative ions, and electrons.

[0109] Previously placed on the deposition-assistance substrate 280 is a carbon nanotube film 281 deposited by a method such as vapor deposition method, laser vaporization

method, arc discharge method, or the like. The bias voltage control power supply 282 applies a negative bias voltage to the deposition-assistance substrate 280. By virtue of the action of the bias voltage, collision ions comprising fullerene positive ions in plasma are provided with acceleration energies near the deposition-assistance substrate 280, and collide with carbon nanotubes on the deposition-assistance substrate. Since collision ions having larger masses collide with carbon nanotubes, the carbon nanotubes are largely deformed and six-membered rings constituting the carbon nanotubes are largely opened. Simultaneously with irradiation of collision ions to the deposited film 281, the TTF vapor deposition means shoots vapor comprising TTF molecules 279 to the deposited film 281. Although the TTF molecules 279 are not ionized, they are moved toward the deposited film 281 by virtue of the shooting action. As TTF molecules collide the deposited film 281,and the carbon nanotubes have been deformed and openings thereof have been enlarged, TTF molecules enter tubular bodies of the carbon nanotubes at a higher probability, thereby increasing a formation efficiency of encapsulating-carbon nanotubes.

[0110] It is possible to measure ion densities, ion energies, and the like of plasma by the plasma prove 273. It is also possible that the bias voltage to be applied to the deposition-assistance substrate 280 is made variable, and the bias voltage value is controlled based on the

values measured by the plasma prove 273, thereby optimizing a production efficiency of encapsulating-carbon nanotubes.

[0111] It is further possible to apply a positive voltage to the deposition-assistance substrate 280 to thereby collide fullerene negative ions as collision ions with the deposited film 281, thereby improving an encapsulation efficiency of encapsulation target substances. In this case, it is unnecessary to generate fullerene positive ions and it is thus unnecessary to intentionally raise a temperature of electrons in plasma, thereby making it unnecessary to use the grid electrode 268 and grid voltage control power supply 269.

[0112] The material film production method of the present invention is not limited to carbon nanotube, and can be applied to situations where an encapsulation target substance is to be encapsulated in another nanotube such as BN nanotube, and where atom(s), molecule(s), or the like as an encapsulation target substance(s) such as TDAE, TMTSF, Pentacene, Tetracene, Anthracene, TCNQ, Alq_3, F_4TCNQ other than TTF is/are to be encapsulated in nanotubes. Collision ions are not limited to fullerene positive ions and fullerene negative ions, and it is also possible to use positive ions such as those of Cs, Fr, or the like, and negative ions such as those of Cl, Br, I, or the like by adopting collision ion generation means.

Embodiment:

[0113] Although the present invention will be

described hereinafter with reference to Examples, the present invention is not limited to such Examples.

[0114] Production Example 1:

(Production Example of Li- encapsulating Fullerene: Control of Ion Density)

There was adopted the production apparatus shown in FIG. 1 comprising the cylindrical stainless vacuum vessel having the electromagnetic coil arranged therearound, to produce Li- encapsulating fullerene. Used as Li and C_{60} as applicable starting materials were Li manufactured by Aldrich and C_{60} manufactured by Frontier Carbon Corporation, respectively.

[0115] The vacuum vessel 1 was evacuated to a degree of vacuum of 4.2×10^{-5}Pa, and the electromagnetic coil 3 was used to generate a magnetic field having a magnetic field strength of 0.2T. The alkali metal sublimation oven 6 was filled with solid Li, and heated to a temperature of 480°C to sublimate the Li, thereby generating an Li gas. The generated Li gas was introduced through the introduction pipe 7 heated to 500°C and shot onto the hot plate 5 having a diameter of 6cm and heated to 2,500°C. Li vapor was ionized on the surface of the hot plate 5, thereby generating a plasma flow comprising positive ions of Li and electrons. The grid electrode 11 was arranged in the course of the plasma flow, which was made of nonmagnetic stainless electroconductive wires having a lattice spacing of 1mm, and the power supply 12 was caused to apply a

control voltage to the grid electrode.

Further, shot into the generated plasma flow and toward the deposition-assistance substrate 18, was C_{60} vapor which was obtained by heating fullerene to 610°C to thereby sublimate it in the fullerene sublimation oven 15. Applied to the deposition-assistance substrate 18 in contact with the plasma flow was a bias voltage of -30V while applying the control voltage to the grid electrode 11 to thereby conduct deposition for about one hour, thereby depositing a thin-film including encapsulating-fullerene on the surface of the deposition-assistance substrate 18.

[0116] The deposited film was collected and washed by pure water to remove Li and Li compound which were not encapsulated, followed by elementary analysis to measure contents of Li and carbon to thereby obtain a content of encapsulating-fullerene.

Elementary Analysis Result:

Control voltage of grid electrode	Content (relative value) of encapsulating-fullerene
-10V	0.8
0V	0.9
10V	1.5
20V	1.2
without voltage application	1

[0117] From the content data of encapsulating-fullerene, it has been shown that a production amount of encapsulating-fullerene can be controlled by providing the grid electrode in the course of a plasma flow and by applying a control voltage to the grid electrode. Concerning the production conditions for the embodiment, it has been shown that the production efficiency of encapsulating-fullerene is maximized when the grid control voltage is +10V.

[0118] Production Example 2:

(Production Example of K-encapsulating Fullerene: Irradiation of Collision Ion)

There was adopted the production apparatus shown in FIG. 3 comprising the cylindrical stainless vacuum vessel having the electromagnetic coil arranged therearound, to produce K-encapsulating fullerene. Used as K and C_{60} as applicable starting materials were K manufactured by Aldrich and C_{60} manufactured by Frontier Carbon Corporation, respectively.

[0119] The vacuum vessel 81 was evacuated to a degree of vacuum of 4.5×10^{-5}Pa, and the electromagnetic coil 83 was used to generate a magnetic field having a magnetic field strength of 0.3T. The alkali metal sublimation oven 86 was filled with solid K, and heated to a temperature of 450°C to sublimate the K, thereby generating a K gas. The generated K gas was introduced through the introduction pipe 87 heated to 480°C and shot onto the hot plate 85

having a diameter of 6cm and heated to 2,500°C. K vapor was ionized on the surface of the hot plate 85, thereby generating a plasma flow comprising positive ions of K and electrons. The grid electrode 91 was arranged in the course of the plasma flow, which was made of nonmagnetic stainless electroconductive wires having a lattice spacing of 1mm, and the power supply 92 was caused to apply a control voltage of +15V to the grid electrode.

Further, introduced into the course of generated plasma was C_{60} vapor obtained by heating fullerene to 630°C to thereby sublimate it by the fullerene oven 93, thereby generating fullerene positive ions 96. Fullerene positive ions were generated so as to be used as collision ions, respectively. Further, shot toward the deposition-assistance substrate 100 was C_{60} vapor obtained by heating fullerene to 600°C to thereby sublimate it by the fullerene sublimation oven 103. Applied to the deposition-assistance substrate 100 in contact with the plasma flow was a bias voltage of -40V to thereby conduct deposition for about two hours, thereby depositing a thin-film including encapsulating-fullerene on the surface of the deposition-assistance substrate 100.

[0120] The deposited film was collected and washed by pure water to remove K and K compound which were not encapsulated, followed by elementary analysis to measure contents of K and carbon to thereby obtain a content of encapsulating-fullerene.

Elementary Analysis Result:

Collision ion	Content (relative value) of encapsulating-fullerene
Used	8
Unused	1

[0121] From the content data of encapsulating-fullerene, it has been shown that a production efficiency of encapsulating-fullerene is improved by irradiating collision ions to material molecules simultaneously with encapsulation target ions.

INDUSTRIAL APPLICABILITY

[0122] As described above, the material film production method and production apparatus according to the present invention are excellent in controllability of irradiating ion density, and can be easily optimized in production condition of material films such as encapsulating-fullerene, hetero-fullerene, and the like. Further, simultaneous irradiation of encapsulation target ions and collision ions is useful for improving a production efficiency of a material film for encapsulating therein encapsulation target atom(s), encapsulation target molecule(s), or the like each having a larger diameter.